A72-30406

NASA TECHNICAL MEMORANDUM NASA TM- 76624

EFFECT OF ALLOYING ON AGING AND HARDENING PROCESSES OF STEEL WITH 20% NICKEL

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(NASA-TM-76624) EFFECTS OF ALLOYING CN AGING AND HARDENING PROCESSES OF STEEL WITH 20% NICKEL (National Aeronautics and Space Administration) 13 p HC A02/MF A01 CSCL 11F

N82-11186

Unclas
G3/26 27779

Translation of "Vliyanie legirovaniya na protsessy stareniya i uprochneniya stali s 20% nikelya", Fizika metallov i metallovedenie, Vol. 33, Feb. 1972, pp. 362-368

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 SEPTEMBER 1981

STANDARD TITLE PAGE

1. Report No. NASA TM- 76624	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle EFFECT OF ALLOYING ON AGING AND HARDENING PROCESSES OF STEEL WITH 20% NICKEL		5. Report Date September 1981
		6. Performing Organization Code
7. Author(s) I. N. Bogachev, N. V. Zvigintsev and T. M. Maslakova		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		11. Contract or Grant No. NASw-3541
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D. C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Vliyanie legirovaniya na protsessy stareniya i uprochneniya stali s 20% nikelya", Fizika metallov i metallovedenie, Vol. 33, Feb. 1972, pp. 362-368.

(A72-30408)

16. Abstract

Measurements of hardness, thermal emf, and electrical resistance were used to study the effects of Co, Mo, Ti and Al contents on aging and hardening processes in Fe 20%Ni steel. It is shown that the effects of these alloying elements differ substantially. Anomalies which arise in the temperature dependence of physical properties due to the presence of cobalt and molybdenum are reduced by the inclusion of titanium and aluminum (and vice versa).

17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified-Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22.

NASA-HQ

EFFECT OF ALLOYING ON AGING AND HARDENING PROCESSES OF STEEL WITH 20% NICKEL

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Studied herein is the effect of alloying on the aging and hardening processes of steel with 20% nickel by means of measurement of the hardness and a number of physical properties. The varying effect of Co, Mo, Ti and Al on these processes is established. /362*

Through the study of the effect of alloying elements on the hardening of Fe—Ni martensite with aging, it was established [1] that the alloying elements may be placed in the following order: Ti, Al, Nb, Mn, Zr, Mo, and so on. The effect of hardening increases sharply with simultaneous alloying with several elements. Cobalt plays a special role in the processes of hardening and aging. By having a favorable effect on the plastic properties, it leads to additional hardening of martensite aging steels. This effect is demonstrated especially strongly in alloys which contain molybdenum [2-5].

Various points of view support the role of cobalt in hardening. The authors of [2,3] think that cobalt, by decreasing the equilibrium solubility of molybdenum in iron and nickel martensite, intensifies the effect of hardening. It is assumed in studies [4,5] that cobalt promotes ordering in the matrix, and thereby increases the effect of hardening of iron-nickel-molybdenum steel.

Studies of the process of breakdown in steel, containing 18% Ni, 8% Co and 6% Mo, by the method of Mossbauer spectroscopy showed [6] that, in the indicated steel, the breakdown process consists of at least two stages, Fe_2Mo forms in the second stage, and cobalt does not take part in these reactions.

*Numbers in the margin indicate pagination in the foreign text.

Studied in the present study is the effect of alloying elements on the aging and hardening processes, according to the change in hardness and a number of physical properties: thermoelectromotive force E, electric resistance ρ.

CHEMICAL COMPOSITION OF STUDIED STEELS

Grade of Steel	Content of Elements, %									
	C	Ni	Co	Mo	Al	Ti	Mn	Si	S	P
N20	0,03	19,5	—	—	—	—	0,1	0,1	0,02	0,01
N20M2	0,03	19,5	—	2,0	—	—	0,1	0,1	0,02	0,01
N20M5	0,03	19,5	—	5,0	—	—	0,1	0,1	0,02	0,01
N20C10	0,03	19,6	10,1	—	—	—	0,1	0,1	0,02	0,01
N20C15	0,03	19,6	15,1	—	—	—	0,1	0,1	0,02	0,01
N20C10M5	0,03	19,55	10,2	5,1	—	—	0,1	0,1	0,02	0,01
N20C10M5TYu	0,03	19,55	10,2	5,15	0,28	1,4	0,1	0,1	0,02	0,01
N20TYu	0,01	19,8	—	—	0,38	1,43	0,18	0,2	0,01	0,03
N20M3TYu	0,01	19,8	—	2,82	0,38	1,13	0,18	0,2	0,01	0,03

The chemical composition of the studied alloys is given in the table. The steels were smelted in an open induction furnace with sequential alloying. The samples were quenched in water after an hour of holding at 900°. Aging was carried out in a salt bath. The methods of measurement of the physical properties did not differ from those described earlier in [7].

Results and Their Discussion /363

Measurements of Hardness. Shown in figure 1 is the dependence of the hardness on the aging temperature (holding of 1 hour) for alloy N20, quenched at 900°C and alloyed with various elements. As is evident from the figure, alloy N20 (without additional alloying) does not harden with aging.

The introduction of 10% Co or 2% Mo leads already to a slight increase in hardness with aging in the 300-450° interval. The maximum increase in hardness (ΔHB=70 kg/mm^2 with 10% Co and 25 kg/mm^2 with 2% Mo) is observed at 400-450°. The effect of hardening increases with an increase in the content of these elements (ΔHB=100 kg/mm^2 with 15% Co and ΔHB=150 kg/mm^2 with 5% Mo); in this case, the maximum of hardening for alloy N20M5 shifts into the region of higher temperatures (550°), which correspond to the

temperatures of formation of molybdenum intermetallic compounds [8].

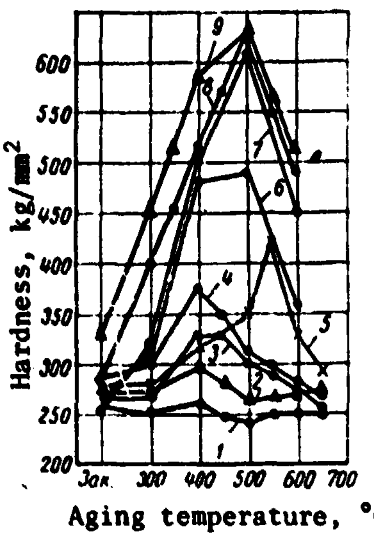

Fig. 1. Dependence of hardness on temperature of aging of quenched Fe—Ni steels:

1-N20; 2-N20M2; 3-N20C10; 4-N20C15; 5-N20M5; 6-N20C10M5; 7-N20TYu; 8-N20M3TYu; 9-N20C10M5TYu.

Thus, both molybdenum and cobalt lead to hardening with aging of Fe—Ni martensite. Combined alloying of steel with molybdenum and cobalt leads to a stronger hardening than separate alloying.

The maximum of hardening with complex alloying with molybdenum and cobalt is observed in the interval 450-500°, that is, at intermediate temperatures of maximum hardening of molybdenum and cobalt steels. The increase in hardness in steel N20C10M5 with aging is equal to 230 kg/mm², which is close to the total increase in hardness of steels N20M5 (ΔHB=150 kg/mm²) and N20C10 (ΔHB=70 kg/mm²). One can conclude from this that hardening of alloy N20, with simultaneous alloying with cobalt and molybdenum, is composed of hardening because of the molybdenum and cobalt. However, the authors of [2] think that hardening of steels, which contain molybdenum and cobalt (N16C15M5 and N16M5), is brought about by the formation of molybdenum intermetallic compounds. The strongest effect of hardening is observed with alloying of alloy N20 with titanium and aluminum (ΔHB=350 kg/mm²).

Additional alloying of alloy N20TYu with molybdenum (3%), as well as molybdenum (5%) and cobalt (10%)[1] together, does not lead

[1]Additional alloying of alloy N20TYu with molybdenum and cobalt makes it necessary to use cold treatment for changing of the alloy into a martensite state (alloy N20C10M5TYu). After cold treatment at 196°, up to 10% γ-phase is contained in the alloy N20C10M5TYu.

to intensification of the effect of hardening: the hardness of alloys N20TYu, N20M3TYu and N20 Cl0M5TYu is roughly at one level after maximum hardening (~600-630 HB).

From here, it follows that, in the alloys N20TYu, N20M3TYu and N20 Cl0M5TYu, Ti and Al are basically responsible for the aging processes, while the contribution of Mo and Co is evidently insignificant.

Observed through electron-diffraction studies of re-aged samples of steels N20TYu and N20M3TYu were only the intermetallic compounds Ni_3Ti [9] in this and other cases. Molybdenum intermetallic compounds are not detected. One may assume that molybdenum does not form with contents of ≤3% of the intermetallic compounds in martensite aging steels. The absence of hardening of the alloy N20M2 at increased temperatures (450-550°) also indicated this fact. The slight hardening of alloy N20M2 at 400° may be associated with the formation of segregations at the defects [10]. With molybdenum contents of ≥5.0%, the formation of molybdenum intermetallic compounds is possible [8]. However, with combined alloying with Mo, Co, Al and Ti, the formation of Mo intermetallic compounds is evidently suppressed, to some extent, as a result of the active formation of Al and Ti intermetallic compounds, and the component part of hardening because of Mo and Co decreases. Conversely, Co and Mo may weaken the effect of hardening because of Al and Ti. /364

Changes in Physical Properties. Also observed in the temperature interval of hardening are anomalous changes in the physical properties. Given in figure 2 are the temperature dependences of the thermoelectromotive force E of the studied alloys. As is evident from the figure, in alloy N20, which does not contain elements which evoke aging, anomalies are not observed in the temperature dependence of E. This is especially evident on the one-hour isochrone—the dotted line. The slight reduction in the thermoelectromotive force with an increase in the aging temperature of this alloy may be explained by a decrease in the density of the

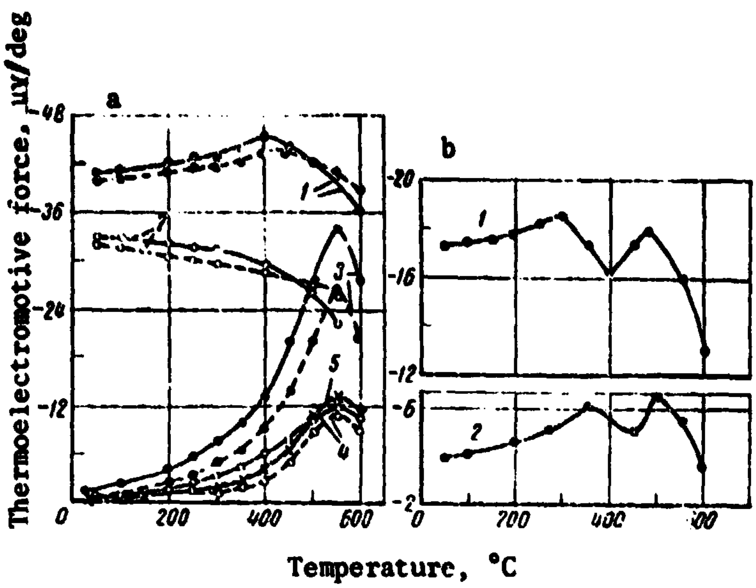

Fig. 2. Temperature dependence and one-hour isochrones (dotted lines) of thermoelectromotive force of quenched Fe—Ni steels:

a) 1-N20C10, 2-N20, 3-N20C10M5, 4-N20M5, 5-N20C10M5TYu; b) 1-N20TYu, 2-N20M3TYu.

dislocations. As compared with N20, the alloy N20C10 has an increased electronegativity, and a maximum appears on the E—T curve at 400-450°. The introduction of 5% Mo into alloy N20 leads to a sharp decrease in the anomalous maximum in the temperature dependence of E at 550°. In this and other cases, the temperatures of the maxima of the thermoelectromotive force coincide with the temperatures of the maxima of hardness.

With complex alloying of alloy N20 with molybdenum and cobalt (N20C10M5), the initial value of E is close to E for alloy N20M5, but the anomalous increase in the thermoelectromotive force on the temperature dependence begins considerably earlier, and at 400°, /365 its increase (with respect to quenched steel) is already two times greater than in alloy N20M5. The maximum is noted also at 550°, just as for alloy N20M5. In magnitude, this maximum is three times greater than in alloy N20M5 (Fig. 2a, Curve 3).

Also observed in the temperature intervals of hardening and the maxima of the thermoelectromotive force of the alloys N20C10,

N20M5 and N20C10M5 are anomalies of a number of other properties: a drop in the electrical resistance, an increase in the modulus of elasticity. The regularities in the change in the temperature dependence of these properties, with varying alloying of alloy N20, are similar to the changes in the thermoelectromotive force. The cited data indicate that both cobalt and molybdenum, which mutually intensify the effect of each other, take part in the aging processes.

Insofar as aging does not take place in alloy N20, one can assume that, with alloying of the indicated alloy with cobalt, molybdenum, or their combination, processes are possible which are inherent to the system Ni—Co, Fe—Co, Ni—Mo, and Fe—Mo. Carried out in study [14] was the study of the ordering in Fe—Co alloys by the method of thermal capacity. The ordering proposed in the indicated study, according to the Fe_3Co type for alloys of iron with 20-30% Co, occurs at temperatures close to the temperatures of the maximum hardening and the anomalies of the physical properties of Fe—Ni—Co alloys, studied in the present study.

The phase Fe_2Mo [13] was observed with aging of Fe—Mo alloys. A similar phase was observed in the Fe—Ni—Mo alloy as well [8]. In the case of alloying of alloy N20 with titanium and aluminum, the change in the thermoelectromotive force, as a function of the temperature, occurs differently than in alloys with cobalt and molybdenum. The E—T curve of steel N20TYu is characterized by extremal points at 300, 400 and 480° C (Fig. 2b, Curve 1). Similar dependences of the thermoelectromotive force on the temperature are obtained by the authors of [11] for steel which is close in composition, as well as by the authors of [12] during the measurement of the thermal capacity of the studied steel (N20TYu).

An additive of 3% Mo to steel N20TYu leads to a reduction in the electronegativity, a decrease in the anomalous effects, and a slight shift of these effects into a region of higher temperatures (Fig. 2b, Curve 2).

By comparing the curve of the temperature dependence of the

thermoelectromotive force of steels N20TYu and N20M3TYu, one may conclude that the anomalies on the indicated curves are brought about by titanium and aluminum. Molybdenum weakens the anomalous effects of the thermoelectromotive force, brought about by titanium and aluminum. In turn, titanium and aluminum, introduced into steel N20C10M5, considerably weaken the anomalous effect in the temperature dependence of the thermoelectromotive force, brought about by additives of molybdenum and cobalt (Curve 5, Fig. 2a).

The one-hour isochrones of the thermoelectromotive force, obtained at room temperature with preliminarily heat treated samples of the studied steels, are similar to the temperature dependence of the thermoelectromotive force of these same steels (Fig. 2a), which is a corroboration of the correctness of the interpretation of the obtained data on the temperature dependence of the thermoelectromotive force. The anomalous effects in the temperature dependence of E are brought about by processes which change the electron density of the alloy.

Kinetics of Aging. Shown in figure 3 are the isotherms of the change in the thermoelectromotive force with aging of the studied steels. For all of the studied aging temperatures, the curves of steels N20M5 and N20C10M5 differ only in the initial period of aging; in the first several minutes, the alloy with cobalt additives has a much greater increase in E. Then, the curves of the thermoelectromotive force run parallel, but the curve for the alloy with cobalt passes higher (Fig. 3a). This indicates that the effect of cobalt shows up only in the initial /366 period of aging. The 400° isotherms also indicate this. For steel N20M5, an increase in E is practically not observed with holdings for up to 18 hours, while a large increase is observed for steel N20C10M5.

The isotherms of steel N20TYu (Fig. 3b), after aging at temperatures below 400° and holdings of up to 20 hours, are characterized by a monotonous decrease in E. At the 400° isotherm of the thermoelectromotive force of steel N20TYu, one can

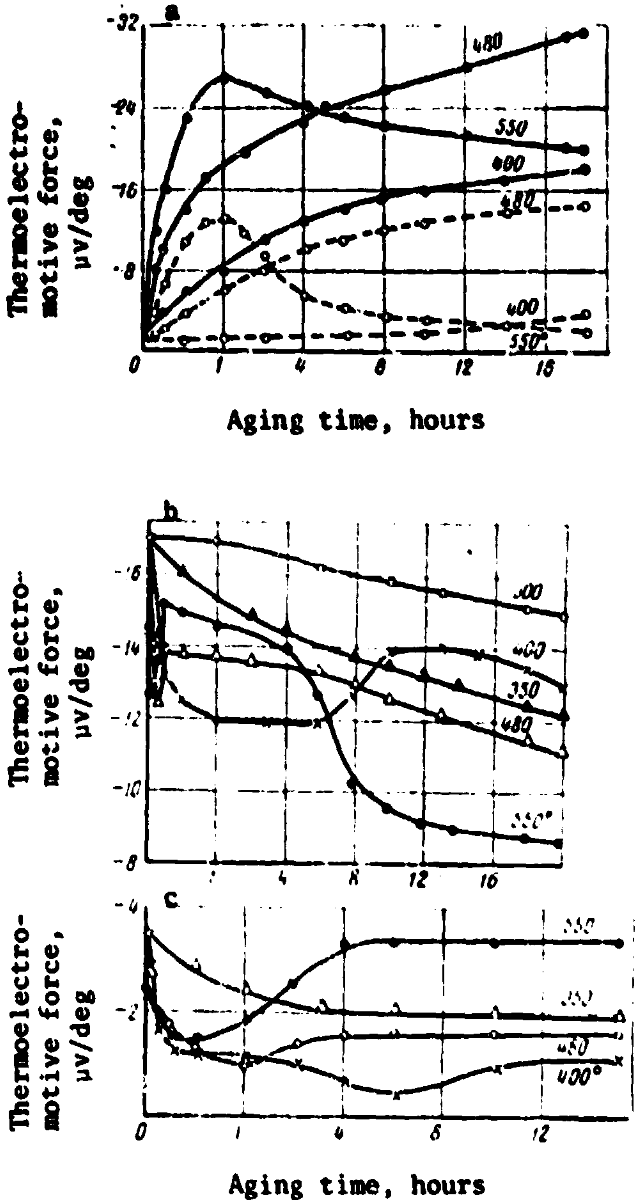

Fig. 3. Kinetics of the change in the thermoelectromotive force in quenched Fe—Ni steels:
a-N20M5 (○), N20C10M5 (●); b-N20TYu; c-N20M3TYu

trace the development, with time, of all the stages of the aging process, observed on the temperature dependence of the thermoelectromotive force of this steel. At 400° in 6 hours, the first stage of aging occurs completely, characterized by a decrease in /367
E. During this period, a considerable hardening is observed. With holding of over 6 hours, the second stage begins, characterized by an increase in E. Additional lines appear on the electron-diffraction patterns during this period, and the electrical re-

sistance and specific volume decrease. With holdings of more than 10 hours, the values of E stabilize. The hardness in this case continues to increase continuously. Consequently, the established equilibrium is dynamic. At higher temperatures of aging, these stages shift in the direction of shorter holdings. Holdings at 480° for over 6 hours lead to a new drop in E, that is, processes of softening begin to develop in the material, but their contribution to the total aging process is still slight, since the hardness continues to be maintained at the previous level. At 550°, holdings of more than 10 minutes even lead to a second decrease in E. A decrease in hardness also corresponds to this.

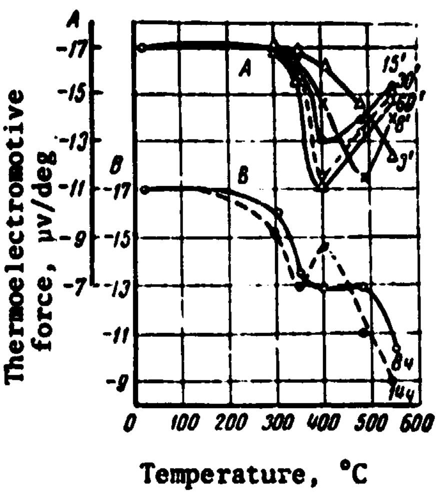

Fig. 4. Dependence of thermoelectromotive force on temperature and time of aging of quenched steel N20TYu.

The isotherms of the thermoelectromotive force of quenched steel N20M3TYu are similar to the isotherms of the thermoelectromotive force of quenched steel N20TYu, but the effects of a change in E are less, and are shifted into the region of higher temperatures (Fig. 3c), which corroborates the assumption of weakening of the role of aluminum and titanium in the aging processes in the presence of molybdenum.

It is evident from the examined isotherms of aging of steels N20TYu and N20M3TYu that, at one and the same temperature, all of the stages of aging may develop. The isochrones, constructed according to the kinetics of aging (Fig. 4, for steel N20TYu) provide an idea of the relative share of the contribution to the aging process of these steels. The isotherms, and, consequently, the isochrones constructed according to them, of each point characterize some equilibrium between the stable and metastable phases, the relative number of which changes continuously with a change in the temperature or time of aging.

Conclusions

1. The aging and hardening processes of Fe—Ni dispersion hardening steels are brought about by both molybdenum, titanium and aluminum, and by cobalt. The effect of these elements on the indicated processes is varied.

2. The anomalies in the temperature dependence of the physical properties, brought about by cobalt and molybdenum, are weakened by titanium and aluminum, and vice versa.

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